THE INFRARED AND RAMAN SPECTRA OF CYCLOPENTANE, CYCLOPENTANE-d_1, AND CYCLOPENTANE-d_{10}

BY

RICHARD GUY INSKEEP

A.B., Miami University, 1944
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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Introduction

The saturated five-membered carbon ring is a unit in many chemical compounds and consequently its structure is of great interest. There is a question as to whether the carbon atoms are at the corners of a regular plane pentagon or whether the carbon ring is warped into a nonplanar form. Kilpatrick, Pitzer and Spitzer have pointed out that if the forces between the hydrogen atoms of adjacent methylene groups are repulsive, they will tend to warp the ring into a nonplanar form. Conversely, the forces resisting changes in the tetrahedral C-C-C bond angles will tend to constrain the ring to a plane.

As cyclopentane is readily adaptable to infrared and Raman spectroscopic techniques, it was decided to attempt to answer this question by re-examining the spectroscopic data, and to strengthen this data by obtaining the spectra of the isotopic molecules cyclopentane-d_1 and cyclopentane-d_{10}.

Experimental

The cyclopentane-d_1 was prepared by the following reaction:

$$C_5H_9Cl \xrightarrow{Mg} C_5H_9MgCl \xrightarrow{DCl} C_5H_9D + MgCl\ (s).$$

The cyclopentane-d_{10} was prepared by the exchange of the hydrogens of cyclopentane in the vapor state with deuterium gas over a catalyst of palladium on charcoal maintained at 200° C.

The Raman spectra of the three compounds were obtained in the liquid state and the infrared spectra from 400 cm^{-1} to 3000 cm^{-1} were obtained in the liquid and vapor state.

Summary

An analysis of the data on the basis of D_{5h} symmetry for cyclopentane was made. This structure was rejected for the following reasons. (1) The observed fundamentals did not indicate a calculated entropy as large as the measured entropy and there was little evidence for a low-lying fundamental (~ 145 cm^{-1}) that would bring this calculated entropy into agreement with the observed value. (2) Some left-over bands were unassigned. (3) The assignment of the infrared-active fundamentals based upon the product rule did not agree with the assignment upon the basis of predicted band contours. (4) The assignment did not agree with past experience with other alicyclic molecules.

A second analysis on the basis of a rigid nonplanar ring of low symmetry (C_S, C_2, or C_1) resolved most of the difficulties found with the D_{5h} assignment except that connected with the entropy. The calculated entropy still did not agree with the measured entropy, although the difference was much smaller. The finding of an as-yet-unobserved frequency at approximately 200 cm^{-1} would bring the two values of the entropy into agreement.

The explanation advanced by Kilpatrick, Pitzer and Spitzer - that one of the out-of-plane modes is a motion of the methylene groups oscillating perpendicular to the σ_h plane (hypothetical), and that the point of maximum displacement of the equilibrium position from the σ_h plane revolves around the ring - is in agreement with all experimental evidence that exists at the present time. There is, however, no direct experimental evidence for this pseudo-rotation.

The experimental data indicates that cyclopentane, though it still follows D_{5h} selection rules rather closely, is of lower symmetry, but the evidence is still inadequate to prove the exact structure.

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VITA

The author was born near East Liberty, Ohio, on March 11, 1923. He attended the local public schools and graduated from Perry Rural High School in 1940. He entered Miami University on a scholarship and graduated from that institution in January 1944.

Following graduation he served as an enlisted man in the United States Naval Reserve. After being discharged from the Naval Reserve in 1945, he worked as a Research Engineer in the fuels research division of Battelle Memorial Institute, Columbus, Ohio.

He then entered the graduate college of the University of Illinois in September 1946, and received a Master of Science in Chemistry in October 1947. While at the University of Illinois he served as part-time teaching assistant in physical chemistry for five semesters. His third year of residence was taken in absentia at Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania.

He is a member of Alpha Chi Sigma and the American Chemical Society.

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